The adsorption of crystal violet by kaolin

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The uptake of crystal violet on kaolin was examined over a pH range of 2·5 to 9·5, adsorption showing an increase with pH. The attainment of equilibrium between adsorbate and adsorbent is shown to be a two-stage process, the first stage being synchronous with the release of magnesium from the kaolin lattice. Evidence is presented that the major mechanism of adsorption is by electrostatic charges arising from cation replacement in the clay lattice, and that charges arising from the amphoteric nature of the aluminium atom of kaolin make little contribution to the overall adsorptive process.

The adsorption by kaolin of promazine has been reported by Sorby, Plein & Benmaman (1966) and of atropine by Ridout (1968a,b). These workers found the adsorption to be pH dependent. So that the mechanism of adsorption might be established, we have examined the uptake by kaolin of a basic substance, crystal violet, under a variety of experimental conditions.

MATERIALS AND METHODS

Crystal violet (reagent grade) was used without further purification.

Light kaolin (B.P. quality) was dried at 100° (3 h), mixed thoroughly and stored in tightly closed containers. The weight mean diameter of the kaolin was 3·3 μm (sedimentation balance), and the surface area 11·2 m² g⁻¹ (nitrogen adsorption: Perkin-Elmer Shell sorptometer, Model 212D).

The effect of pH on the adsorption of crystal violet by kaolin

To flasks containing kaolin (2 g) was added 100 ml of a solution of crystal violet (50 mg/100 ml) in citrate–phosphate–borate buffers of varying pH (Teorell & Stenhagen, 1938). The flasks were equilibrated at 24° (12 h). Samples were removed from each flask and centrifuged at 10 000 rev/min (2 min) and the concentration of crystal violet determined spectrophotometrically at 590 nm. Beer's law was obeyed over the range of concentrations used.

Adsorption isotherms of crystal violet on kaolin were determined in the same way at a range of pH values and using crystal violet concentrations ranging from 40–60 mg/100 ml. Equilibration and determination of the dye in the supernatant were carried out as above and the adsorption isotherms constructed.

Leaching of inorganic ions from kaolin

Measured amounts of N/100 sodium hydroxide solution were diluted to 100 ml with water, the sodium content measured by flame photometry, kaolin (10 g) was added and the whole allowed to equilibrate overnight. The sodium content of the supernatant was then determined. The experiments were then repeated incorporating EDTA in the mixture and the supernatant assayed for aluminium by complexation with Alizarin S (Barton, 1948) and for magnesium and calcium by atomic absorption spectrophotometry.

RESULTS

Preliminary experiments showed that on prolonged shaking with water, kaolin released an unknown substance which absorbed light in the ultraviolet region of the spectrum. For this reason, crystal violet was chosen as adsorbate since it can be readily determined in the visible region of the spectrum with no interference from substances leached from kaolin. The colour of crystal violet fades gradually, particularly at high pH (Turgeon & LaMer, 1952), and this has been attributed to a reaction between the dye and hydroxyl ions to give the corresponding carbinol, which is appreciably less soluble in water than crystal violet. Though Turgeon and LaMer have described this as a second order reaction, the present work indicates that first order kinetics may be applied to a first approximation and that the rate of fading (k) at various pH values may be described by the equation:

$$\log k = -0.392 - \frac{14.85}{\text{pH}}$$

All experimentally determined concentrations of crystal violet were thus corrected for time and pH effects by application of this equation.

Data obtained from adsorption experiments were shown to fit the Langmuir equation:

$$\frac{C}{x/m} = \frac{1}{ab} + \frac{1}{b} \cdot C$$

where x = weight of adsorbate (mg) adsorbed by m g of adsorbent; C = the equilibration concentration (mg/100 ml); a,b are constants. A plot of $\frac{C}{x/m}$ against C, gave a straight line with slope 1/b, changes in the value of which provided a useful indication of the extent to which adsorption changed with experimental conditions.

The increase in uptake of crystal violet on kaolin with increasing pH is shown in Fig. 1, and values of "1/b" (g/mg) derived from isotherms determined at pH values of 4·4, 5·8, 6·8, 7·4, 8·1 are: 0·0450, 0·0448, 0·0416, 0·0409, 0·0378 respectively. It has
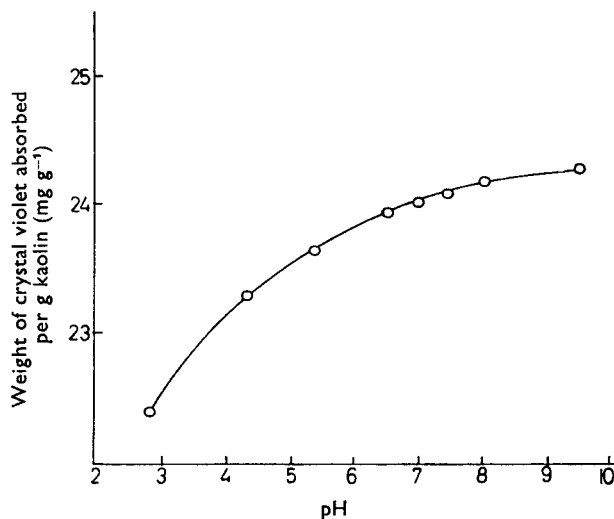

FIG. 1. The uptake of crystal violet on kaolin at a range of pH values.

been claimed (Ridout, 1968) that the uptake of atropine by kaolin can be represented by two straight lines of significantly different slopes because of the heterogeneous nature of the kaolin surface. No evidence of a two-stage Langmuir isotherm was found in the present work.

The rate of crystal violet uptake on kaolin shows a stepped curve before equilibrium is finally established after about 0·5 h (Fig. 2). No such deviation was reported (Ridout, 1968a) for the adsorption of atropine by kaolin and, since the adsorption curve before the "step" is non-linear, it is difficult to prove the validity of this step by standard statistical techniques. Nevertheless, numerous replicate determinations invariably showed the presence of this irregularity, and it is possible to explain it by reference to the molecular structure of kaolin.
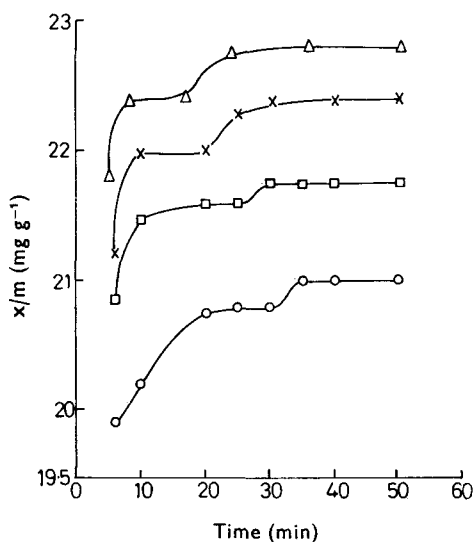

FIG. 2. The rate of uptake of crystal violet on kaolin. ○, pH 5·8; □, pH 6·6; ×, pH 7·7 △, pH 8·4.

DISCUSSION

The molecular structure of kaolin, $Al_4Si_4O_{10}(OH)_8$, is composed of two basic units (Brindley & Robinson, 1946; Brindley, 1951). One is an octahedron of oxygen atoms (or hydroxyl groups) surrounding a central aluminium atom, with several such octahedra, sharing the oxygen atoms of identical adjacent structures, joined together to form a continuous sheet. The second unit is composed of four oxygen atoms situated at the corners of a regular tetrahedron, with a silicon atom in the centre. The atoms at the base of the tetrahedra are shared by neighbouring modules, and the two basic units are joined so that the apices of the tetrahedra and the top layer of the octahedra form a common plane (Gruner, 1932).

The adsorptive capacity of kaolin has been attributed to electrostatic charges which may arise by two different mechanisms. Grim (1953) has suggested that such charges may arise from broken bonds at the edge of the kaolin particle. Charges in the tetrahedral silicon layer will invariably be positive, irrespective of pH, while those in the octahedral aluminium layer will vary with pH, being positive at low pH and

negative at higher pH values. Thus at low pH, the entire edge carries a positive charge which will become less positive (and may even become negative) as the pH increases.

On the other hand, Schofield & Samson (1953) have suggested that the major site of electrostatic charges is on the face of the kaolin particle, caused by the iso-morphous replacement of silicon and aluminium atoms in the tetrahedral and octa-hedral layers respectively by aluminium and magnesium (and to a lesser extent, calcium). Where the replacing atoms are mono or divalent, the resulting charges will invariably be negative and because the area of the faces is greater than that of the edges (Mering, Matthieu-Sicard & others, 1953), the overall charge on the particle is likely to be negative. Whatever the site of the charge, it is externally compensated by attraction of cations to the kaolin surface.

In the pH range studied, the molecular form of crystal violet is an ion bearing one positive charge (Finar, 1963), which suggests attachment to a negative site on the kaolin particle. The increase in the amount of adsorption with pH may then be due to two factors:

(i) An increase in the density of the negative charge on the edge of the kaolin due to the charge on the aluminium atoms at the edge changing from positive to negative. The pH at which the charge on hydrated alumina is reversed (the zero point of charge) has been reported by van Schuylenborgh & Sanger (1949) as ranging from pH 2·2 to 5·6, depending on the physical structure of the alumina. Though similar information for kaolin has not been published, electrophoresis and flocculation measurements (unpublished observations) indicate a zero point of charge in the range 4·9 to 5·0. This is unlikely to account for the marked increase in adsorption at higher pH values.

(ii) The increased concentration of sodium hydroxide in the system needed to achieve high pH values promotes replacement on the exterior of the clay lattice of the charge-compensating cations of magnesium, calcium and possibly aluminium, by sodium ions. This represents a cation exchange mechanism. The resulting electrical imbalance in the clay lattice increases the negative charge on the particle as a whole and consequently favours the adsorption of a positively charged ion such as crystal violet.

Though aluminium was considered to be the most likely atom to be replaced by sodium, kaolin is associated with appreciable amounts of magnesium and calcium by isomorphous replacement. Since it is probably easier for monovalent sodium to exchange with a divalent rather than a trivalent species, all the above possibilities of ion exchange were examined.

Fig. 3 shows the change in aluminium concentration with change in sodium hydroxide concentration. In this the amount of aluminium leached into the super-natant is negligible between pH 4 and pH 9.

By contrast the appearance of cations such as magnesium in the supernatant shows a marked increase with pH, and it is concluded that ion exchange is the main adsorptive process. Though it is recognized that this mechanism may involve several ionic species, the release of magnesium was examined because of the ease with which small changes in concentration of this ion can be determined. Fig. 4 shows that the attainment of a maximum magnesium concentration in the supernatant is synchronous with the first plateau of the adsorption curve of crystal violet on kaolin (Fig. 2). The second plateau of the latter is apparently unconnected with magnesium
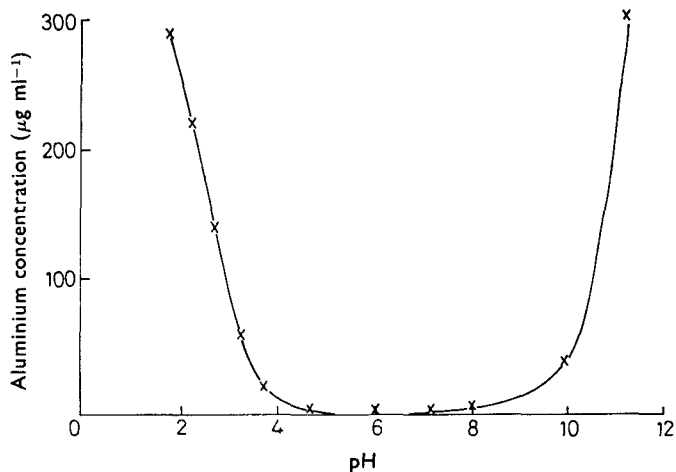
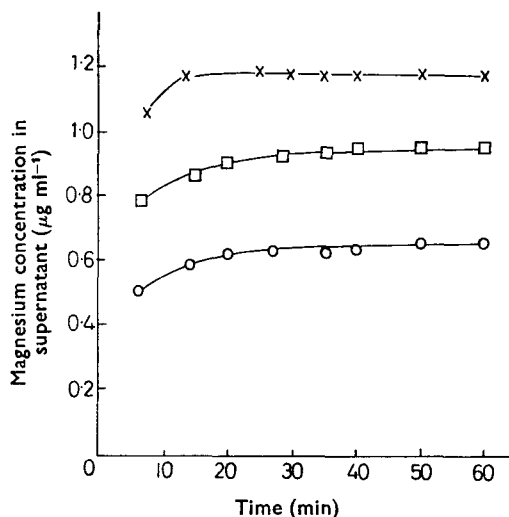FIG. 3. Variation in supernatant concentration of aluminium with pH.

FIG. 4. The rate of leaching of magnesium from kaolin. $\odot$, pH 5·8; $\square$, pH 7·0; $\times$, pH 8·0.

exchange and marks completion of true physical adsorption by intermolecular attractive forces.

Ridout has suggested that the marked increase in the adsorption of atropine sulphate on to kaolin with increase in pH is due to the increase in the density of the negative charge on the edge of the kaolin particle, the amount of adsorption on the face of the particle being constant. However, this explanation must be viewed with caution since: (i) If the zero point of charge on the aluminium atom is in the region of pH 5, most of the aluminium atoms on the edge of the particle will bear a negative charge in the pH range 7 to 9, yet adsorption is still increasing at this point. (ii) The surface area of the edge of the kaolin particle is much smaller than the area of the faces. We have found that electron micrographs of shadowed kaolin indicate an edge to face area ratio of 1 to 14. (iii) The rate of uptake of crystal violet bears a

striking resemblance to the rate of release of magnesium from the clay by ion exchange.

Thus it is concluded that the major mechanism for the adsorption of bases on to kaolin is by electrostatic charges arising from cation replacement in the clay lattice. Such adsorption can take place either on the faces or the edge of the kaolin particle. It is considered that charges arising from the amphoteric nature of the aluminium atom make a relatively small contribution to the total adsorptive process.

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